

Composition and technology of 18th century high magnesia faïences from Fulda

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In 1996, archaeological excavations close to the ancient Fulda faïence manufacture site unearthed a rich deposit of faïence wastes (biscuits, faïences, technical ceramics). The manufacture was founded in 1741 by Prince Abbot Amand von Buseck and closed down in 1761. This first archaeometric study of a German faïence manufacture included 31 samples produced between 1742 and 1760. Analytical techniques were optical microscopy, X-ray fluorescence, X-ray diffraction and scanning electron microscopy, coupled to an energy-dispersive X-ray spectrometer. Biscuits and faïences are MgO- (5–13 wt.%) and CaO-rich (9–20 wt.%), easily distinguishable from the two French Mg-rich productions of Granges-le-Bourg and Lunéville that we know today. Three samples show high P₂O₅ (2.6–3.3 wt.%). Such unusual concentrations are not due to the admixing of crushed bones to the clay during processing, or to one of the well-known post-firing secondary contamination processes, but are caused by the presence of sharp edged, rhomboedric grains with sizes around 20–30 µm and an overall chemical composition of apatite. These fragments are interpreted to be remnants of primary phosphoritic elements, present *ab initio* in the clay, and give some hints as to the origin of the raw materials used. Phosphoritic layers can be found in the German Trias, mostly in dolomitic marls of the Middle Keuper. Such marls form the basement on which Fulda is built and could easily have been extracted by the Fulda manufacture. The high MgO values of the faïences can therefore be linked to the presence of dolomitic grains in the plastic raw material, corroborated by the positive MgO/CaO correlation. Firing temperatures of the faïences were, according to their XRD patterns, mostly between 950 and 1050 °C.

1. Introduction

1.1. German faïence manufactures

Faïence is a tin-glazed pottery, i. e. a type of earthenware covered with a lead-alkali glaze to which tin oxide (cassiterite, SnO₂) has been added as an opacifier. According to Rosen (2009, p. 83) the term “faïence” appeared for the first time on May 25, 1601 in archival sources of Nevers as “vessele de fayance” (crockery in fayance). In 1604, the ceramist Jean-Baptiste Conrade was labelled “sculpteur en terre de fayence” (sculptor of fayence earth) (Rosen, 2000). The oldest faïence manufacture in what is presently Germany is Hanau (Fig. 1), founded in 1661 by Dutch protestant fugitives, forced to leave their homeland on the account of their religion (Merk, 1979; Stasch, 2005a, 2005b). Five other manufactures were set up before 1699, and more than 80 new ones in the 18th century (Klein, 1962, 1975; Frégnac, 1976). The manufacture in Fulda was started in 1741 by Prince Abbot Amand von

Buseck who reigned from 1737 to 1756, from 1752 as Prince Bishop (Steen, 1994; Stasch, 2005a, 2005b). The ultimate goal was not to make faïence, but porcelain, as clearly claimed by the Prince Abbot “.. habe 1742 eine Porzellanfabrik in der Residenzstadt angefangen und dort die nötigen Öfen installiert” (I founded in 1742 a porcelain manufacture in the town of residence and built there the necessary kilns). Adam Friedrich von Löwenfinck (1714–1754), painter in porcelain in Meissen (1727–1736), became the first director of the Fulda manufacture; he left Meissen in 1736 first for the Bayreuth manufacture and then for Ansbach. This is where, around 1737–1740, he successfully transferred the technique of porcelain overglaze enamel painting, invented in Meissen and applied since 1710, onto faïence objects (Stasch, 2005b). In Fulda, the early ceramic products decorated with the inglaze technique are easy to recognize because of their ink blue colour lined with manganese (Stoehr, 1920, pp. 329, 375) painted by Christian Müller (Stasch, 2005b, p. 25), cf. Fig. 2a. Certain objects, by the quality of their onglaze polychrome hand decoration, can be attributed to A. F. von Löwenfinck, even though the signature is missing (Wark, 1956; Ducret, 1971, 1983; Rückert, 1990; Surhone et al., 2010), such as the famous vase with lid (Klein, 1993, plate XI) or the table-centre with the “von Fechenbach” coat of arms (Fig. 2c). A. F. von

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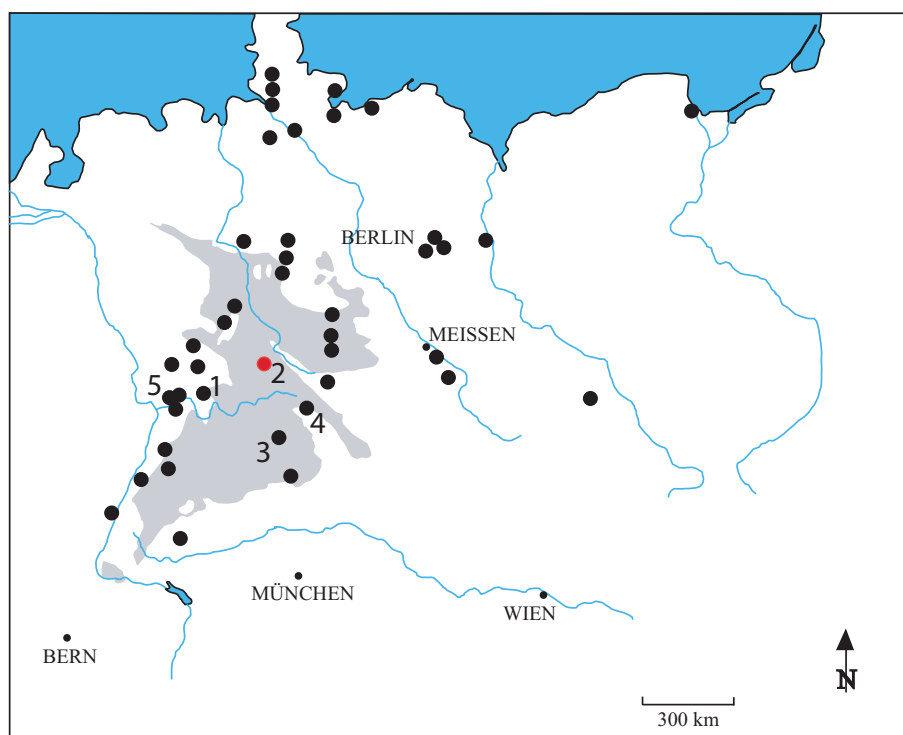


Fig. 1. Map of important German faience manufactures (large dots) of the 17th to 19th centuries, redrawn from Klein (1975). 1 = Hanau, 2 = Fulda, 3 = Bayreuth, 4 = Ansbach, 5 = Höchst. Triassic terrains (Bederke and Wunderlich, 1968) are shown in grey. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Löwenfinck left the manufacture in 1744 to go to Höchst (Ducret, 1971). Fulda kept up its excellent reputation thanks to the commitment of other painters such as Josef Philipp Dannhöffer, Georg Friedrich Hess, and Ignaz Hess. The faience production came to an end in 1760 because of the Seven Years' War (Stasch, 2005a). Four years later, in 1764, a porcelain manufacture was set up in the buildings occupied by the former factory by Prince Bishop Heinrich von Bibra (active from 1759 to 1788). It was shut down in 1789 (Ducret, 1971; Fritzsche and Stasch, 1994; Ullrich and Ballmaier, 2002; Stasch, 2005a, 2005b).

1.2. Production technique

There is no archival documentation about Fulda's faience production technique or about the site of the extracted clays. The first director of the manufacture (1741–1744), A. F. von Löwenfinck, probably learned the faience technique during his stay in the manufactures of Ansbach and Bayreuth. Summaries of the faience technique used in 18th century France and the Netherlands, most probably applied in Germany too, were published by Rosen (1995, 2009), Maggetti (2007, 2012) and Lambooy (2013).

The following short resumé is taken from Heimann and Maggetti (2014, chapter 13): tin-glazed pottery is manufactured from CaO-rich clays in several production steps. After forming and drying, the green ceramic body will be fired in a kiln at maximum temperatures of 900–950 °C (bisque firing). During firing water and other volatile compounds will evaporate. The so-called bisques or biscuits will then be dipped in aqueous glaze slurry. The still porous ceramic body soaks up water from the adhering powdery glaze layer and thus fixes the latter to its surface. If a white product is desired, the ware will be contained, after a short second drying step, in tightly fitting refractory capsules (saggars) and glaze (glost)-fired at approximately 950–1050 °C. For decorated ware, the so-called inglaze colours are painted directly on the dry tin glaze layer prior to glaze firing. This is a rather tricky process as the painted decoration can be corrected only with difficulties since the colour

pigments are readily absorbed by the dry, white glaze powder. When corrections are required the faulty part must be carefully scraped off and the glaze including the colour pigments reapplied. The inglaze colour pigments consisting of powdered crystalline matter or frit glass will be ground together with water and a binder, for example starch. During glaze firing the pigment particles are being coated by a thin sheath of molten glaze and subsequently either dissolved in the glaze, remain as insoluble crystallites, or precipitated as colloidal phase. Since only selected metal oxides survive the high temperatures of the glaze firing the colour palette are blue, brown, yellow, green, red, black, pink and white.

After glaze firing the white or coloured ceramic can be further decorated with differently coloured overglaze (enamel) pigments, i. e. coloured glassy powders. In this case necessary corrections can easily be accomplished since the enamel colours are suspended in volatile oils such as mixtures of turpentine and linseed oil that are applied with a brush to the smooth glaze surface. Overglaze colours generally possess a lower melting temperature compared to the inglaze colours. The enamel pigments are fixed to the glaze surface by a third firing step, also called as colour firing in a muffle kiln at 600–800 °C whereby the pigment particles sink only slightly into the carrier glaze. Since many more metal oxide pigments will be stable at the low temperature of the third firing the colour palette becomes substantially richer.

1.3. Archaeometric analyses and aim of this study

No archaeometric studies were undertaken on German faïences up to now, with one exception: a single blue, black and white decorated shard from Fulda, studied with scanning electron microscopy, which revealed its richness in silica and calcia (Steen, 1994). The present study was therefore undertaken to: (1) define the chemical characteristics of a corpus which would be representative of the Fulda faience in order to create the first reference group for German faience; and (2) define the mineralogical and technological characteristics of this same corpus in order to circumscribe the technique used in Fulda.

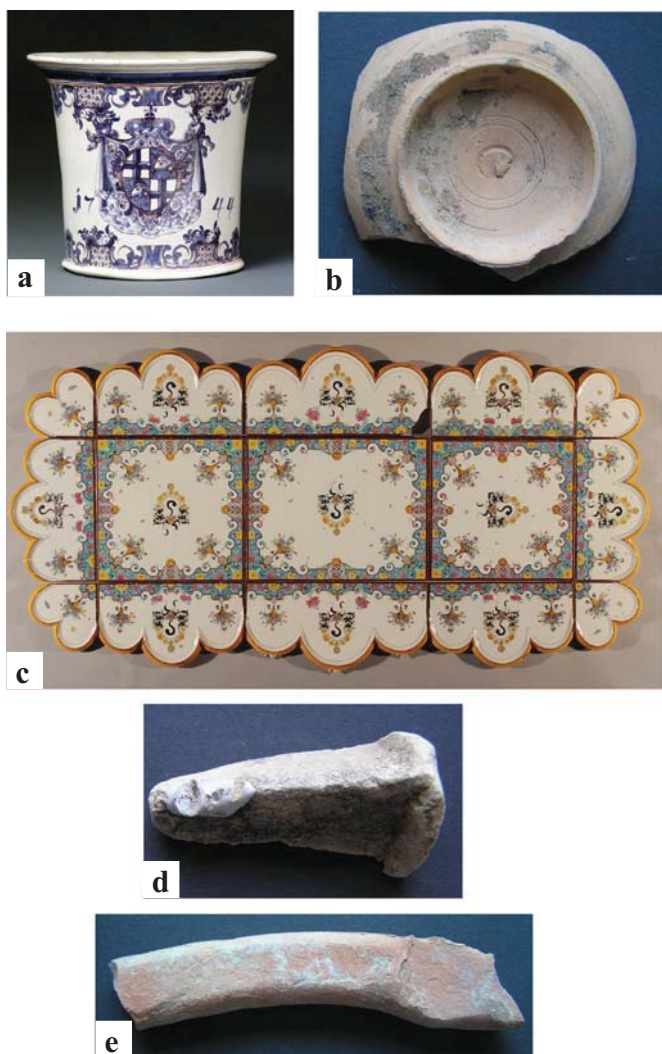


Fig. 2. A selection of the studied objects. (a) Intact plant pot with the coat of arms of Prince Abbot Amand von Buseck (1737–1756) and the year 1744, inglaze polychrome decoration by Christian Müller, height: 20.5 cm, Vonderau Museum Fulda IV D 24, Stasch (2005b, p. 25), analogon to sample FUL 4; (b) biscuit, diam. 5.5 cm, FUL 19; (c) table-centre, onglaze (enamel) polychrome decoration (probably by Adam Friedrich von Löwenfinck) with the coat of arms of the family “von Fechenbach”, rectangular plates: 45 × 45 cm, FUL 32; (d) triangular nail-like saggar pin with adhering tin glaze, length: 5 cm, FUL 23; and (e) accot, length: 8.5 cm, FUL 25.

2. Experimental

2.1. Objects and sampling strategy

The excavation undertaken in 1984 in Fulda's castle garden and the rescue excavation of 1996 brought to light hundreds of faïence shards, from all stages of production, as well as technical ceramics. In 1984, many plant pot shards with the coat of arms of Prince Abbot Amand von Buseck were found, indicating a continuous production of this type of faïence between 1742 and 1749. In 1996, archaeologists excavated some parts of Heinrich von-Bibra Square, in front of the main post office in Fulda, built close to the old faïence/porcelain manufacture, demolished in 1914. A total of 40 objects were studied (Tables 1 and 2, Fig. 2). Twenty-four samples belong to ceramic pieces (12 inglaze decorated faïences, 1 overglaze decorated faïence, 11 biscuits), eight samples to technical ceramics, i. e. 4 saggar pins and 4 accots (= lumps of fired clay), and eight samples are clays. The latter were collected outside of the densely built city, based on the geological

map of Fulda and their description (Bücking, 1911, 1912), mostly in the superficial clayey soils of the meadows and fields southeast of Fulda, with only two specimens (FUL 39, 40) from the compact clayey bedrock (Fig. 3).

2.2. Sample preparation

After careful removal of the glaze and the possibly contaminated unglazed other surfaces with a saw, samples of 1.9–13.5 g were obtained from 39 ceramic pieces and ground in a tungsten carbide mill. If available, subsamples from broken objects were used for scanning electron microscopic (SEM) analyses. Only a small chip could be taken from FUL 32, enough to make a SEM tablet. About 1–2 kg per clay was collected at various depths (Table 2), and 50–100 g dry material was used for the analyses.

2.3. Analytical methods

2.3.1. Chemical composition by X-ray fluorescence analysis (XRFA)

Two grams of powdered sample was calcined at 900 °C for 1 h to obtain the loss on ignition (LOI). 0.700 g of calcined powder was carefully mixed with 6.650 g of MERCK spectromelt A10 ($\text{Li}_2\text{B}_4\text{O}_7$) and 0.350 g of MERCK LiF. This mixture was put into a platinum crucible and melted at 1150 °C for 10 min (Philips® PERL X-2) in order to obtain glassy tablets. These were analysed for major, minor and trace elements using a Philips® PW 2400 wavelength-dispersive spectrometer (Rhodium tube, 60 kV and 30 mA). Calibration was made on 40 international standards (BCR, DTS, PCC, BHVO, QLO, RGM, SCO, BIR, DNC, W-2, SY-2, GA, GH, Mica-Mg, UB-N, DT-N, GS-N, FK-N, AN-G, BE-N, JG-1, JG-1a, JG-2, JG-3, JB-1, JB-1a, JB-2, JB-3, JR-1, JR-2, JA-2, JA-3, JF-1, JF-2, JP-1, JGb-1, NIM-G, NIM-L, NIM-N, NIM-S). Oxides were calculated relative to the standards. Cu- and Pb-concentrations for some clays are low, approaching detection limits. Accuracy and precision were checked using the laboratory reference sample RT. Error has been evaluated by many repetitive measurements of this internal standard to be less than 5% for all elements analysed.

2.3.2. Mineralogical analyses by X-ray diffractometry (XRD)

The mineralogical composition was determined on the powdered samples through powder X-ray diffraction using a Philips® PW 1800 diffractometer ($\text{CuK}\alpha$, 40 kV, 40 mA, 2θ 2–65°, measuring time 1 s/step).

2.3.3. Scanning electron microscopy (SEM)

Backscattered electron images (BSE) were collected with a scintillator type detector out of polished samples, using a Philips® FEI XL30 Sirion FEG electron scanning microscope. The samples were mounted in an epoxy block, flatly polished with a 0.5 μm diamond paste and then coated with a thin carbon layer. Chemical compositions were determined by energy-dispersive X-ray spectrometry (EDS), operated at a beam acceleration voltage at 20 kV and a beam current of 6.5 nA. Standardless quantification was performed using an EDAX-ZAF correction procedure of the intensities, using spot analyses (2 μm diameter) as well as larger area analyses of homogeneous areas. The detection limits for most elements were about 0.2 wt.%. The reliability of the results was proved by measuring well known glass and mineral standards (DLH2, Corning A–D and Plagioclase). The relative mean deviation for major and minor oxide components was 2% for concentrations in the range of 20–100 wt.%, 4% for 5–20 wt.%, 10–20% for 1–5 wt.% and >50% for <1 wt.%.

2.3.4. Statistics

Factor analysis (principal component analysis PCA, Fig. 6c) was performed with log data of 18 variables (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , Na_2O , K_2O , Ba, Cr, Cu, Nb, Ni, Rb, Sr, Y, Zn, Zr) as determined by

Table 1
Description of the 32 ceramic fragments.

No. An.	Excavation	Form	Type	Decoration	Date
FUL 1	EV 84	Plant pot	Faïence	Inglaze polychrome decoration (black, blue and violet)	1748
FUL 2	EV 84	Plant pot	Faïence	Inglaze polychrome decoration (black, blue and violet)	1743
FUL 3	EV 84	Plant pot	Faïence	Inglaze polychrome decoration (black, blue and violet)	1742
FUL 4	EV 84	Plant pot	Faïence	Inglaze polychrome decoration (black, blue and violet)	1744
FUL 5	EV 84	Plant pot	Faïence	Inglaze polychrome decoration (black, blue and violet)	1745
FUL 6	EV 84	Plant pot	Faïence	Inglaze polychrome decoration (black, blue and violet)	1747
FUL 7	EV 84	Plant pot	Faïence	Inglaze polychrome decoration (black, blue and violet)	
FUL 8	EV 84	Plant pot	Faïence	Inglaze polychrome decoration (black, blue and violet)	
FUL 9	EV 84	Plant pot	Faïence	Inglaze polychrome decoration (black, blue and violet)	
FUL 10	EV 84	Plant pot	Faïence	Inglaze polychrome decoration (black, blue and violet)	
FUL 11	EXXVII, 1996	Jug	Biscuit		before 1755
FUL 12	EXXVII, 1996	Plate	Biscuit		before 1755
FUL 13	EXXVII, 1996	Dish	Biscuit		before 1755
FUL 14	EXXVII, 1996	Plate	Biscuit		before 1755
FUL 15	EXXVII, 1996	Dish	Biscuit		before 1755
FUL 16	EXXVII, 1996	Saggar pin			
FUL 17	EXXVII, 1996	Jug	Biscuit		before 1755
FUL 18	EXXVII, 1996	Plate	Biscuit		before 1755
FUL 19	EXXVII, 1996	Bowl	Biscuit		before 1755
FUL 20	EXXVII, 1996	Bowl	Biscuit		before 1755
FUL 21	EXXVII, 1996	Handle for a beer jug	Biscuit		before 1755
FUL 22	EXXVII, 1996	Handle	Biscuit		before 1755
FUL 23	EXXVII, 1996	Saggar pin		Adherent white opaque white tin glaze	
FUL 24	EXXVII, 1996	Saggar pin			
FUL 25	EXXVII, 1996	Accot			
FUL 26	EXXVII, 1996	Accot			
FUL 27	EXXVII, 1996	Accot			
FUL 28	EXXVII, 1996	Accot			
FUL 29	EXXVII, 1996	Saggar pin			
FUL 30	FV, 83 B2	Dish or plate	Faïence	Inglaze polychrome decoration (blue and violet), Mark FD	before 1760
FUL 31	FV, 83 B2	Plate	Faïence	Inglaze spray decoration (violet)	before 1760
FUL 32		Table-centre	Faïence	Overglaze (enamel) polychrome decoration. Coat of arms "von Fechenbach". Painting most probably by A. F. v. Löwenfinck.	before 1745

XRFA using the program SPSS 16 and following the rules outlined by Baxter (1994, 2003).

3. Results

3.1. Ceramic bodies

The analysed shards are rich in magnesium (Fig. 4c). FUL 32, analysed by SEM-EDS, has comparable 8 wt.% MgO (Table 3). FUL 2, FUL 4 and FUL 31 are rich in P_2O_5 (Table 3). The faïences can further be separated into two groups, according to their TiO_2 , Cr, Ni and Rb contents, as shown for instance in Fig. 4a and e where a small group of four faïences (FUL 1, 5, 7, 9), clustering tightly with the technical ceramics, are well distinguished from a homogeneous group of eight faïences. All faïences, two biscuits and four technical ceramics, have lead concentrations >500 ppm (Table 3). FUL 27 is very rich in CaO, FUL 30 and FUL 31 show the highest Cr-contents, FUL 18 has the highest Sr-value, and three samples show Zn values >150 ppm (Fig. 4g).

The bodies have a serial distribution (Maggetti, 1994) of their non-plastic inclusions. These pertain to three major kinds, i.e. quartz, orthoclase and coarse clay mineral, embedded in a fine-grained matrix (Fig. 5a, b). Quartz and orthoclase fragments show angular to subangular shapes. Maximum sizes are between 20 and 40 μm . SEM-EDS analyses of the brighter tiny crystals in the matrix (Fig. 5b) are consistent with Ca-silicates such as wollastonite or anorthite crystallized during firing (Maggetti, 1982; Maniatis et al., 1983; Duminuco et al., 1996; Riccardi et al., 1999; Cultrone et al., 2001). Irregularly shaped pores, often with rhomboedric outlines, correspond to primary particles rich in MgO, i.e. dolomite $CaMg(CO_3)_2$ having reacted with the clay paste during the firing (Fig. 5a, f). Calcium is homogeneously distributed throughout the bodies (Fig. 5e). The microstructural aspect of the sample FUL 31, one of the three shards rich in P_2O_5 , is heterogeneous. It

shows normal-looking areas similar to those in other pieces (Fig. 5a), but also domains with blurred contours and edges, often rich in rhomboedric-shaped crystals (Fig. 5c). Phosphorous is concentrated in these crystals (Table 4).

The studied ceramic samples can be assigned, as shown by their X-ray diffractograms, to two different mineral associations:

- (a) Illite (110) + α -Quartz \pm plagioclase \pm gehlenite \pm diopside \pm hematite \pm calcite (FUL 7, 11, 13, 17, 18, 21, 25, 26).
- (b) α -Quartz + plagioclase + diopside + hematite \pm gehlenite + calcite (FUL 1–6, 8, 9, 10, 12, 14–16, 19, 20, 22–24, 27–31).

Calcite is either a pre-firing phase, in association (a), or a post-firing, secondary phase in association (b) (Maggetti, 1994), as revealed by optical microscopy analysis.

3.2. Clays

The MgO-contents of the eight clays show a wide scatter (Fig. 4c). The superficial clays have, with one exception (FUL 41), low magnesium concentrations (<5 wt.% MgO), contrasting with the MgO-richer bed-rock clays FUL 39, 40.

According to the X-ray diffraction study the eight clay samples can be classified as follows:

- (c) Illite + quartz + plagioclase + orthoclase \pm kaolinite: FUL 37, 42, 43
- (d) Illite + quartz + plagioclase + orthoclase + calcite: FUL 38
- (e) Kaolinite + illite + plagioclase + orthoclase + calcite: FUL 41, 44
- (f) Kaolinite + illite + quartz + dolomite + calcite: FUL 39, 40.

Table 2
Description of the 8 clay samples.

No. An.	Age	Provenance	Coordinates
FUL 37	Middle Keuper	South of Künzell, superficial clay from a field	⁵ 50E 550/ ⁵⁵ 97N 900
FUL 38	Middle Keuper	East of Edeltzell, superficial clay from a field	⁵ 50E 820/ ⁵⁵ 97N 550
FUL 39	Lower Keuper	Southwest corner of the sportsground Bachrain/Künzell, schistose and hard clay in 1 m depth	⁵ 50E 220/ ⁵⁵ 98N 150
FUL 40	Lower Keuper	Southwest corner of the sportsground Bachrain/Künzell, schistose and hard clay in 2 m depth	⁵ 50E 220/ ⁵⁵ 98N 150
FUL 41	Middle Keuper	Southwest of the sportsground Bachrain/Künzell, superficial clay from a field	⁵ 50E 080/ ⁵⁵ 98N 160
FUL 42	Upper Buntsandstein	North of Edeltzell, superficial clay from a field	⁵ 49E 880/ ⁵⁵ 97N 860
FUL 43	Upper Buntsandstein	North of Edeltzell, superficial clay from a field	⁵ 49E 800/ ⁵⁵ 98N 000
FUL 44	Diluvium	Northwest of the tree avenue to the castle <i>Fasanerie</i> , clay in 0.4 m depth of the temporary open space for the construction of the gas-pipe Russia–Germany	⁵ 49E 400/ ⁵⁵ 95N 350

4. Discussion

4.1. Mobility of chemical elements

It is well known that shards can change chemical composition through the migration of chemical elements after firing. This phenomenon could

have applied to the shards buried under ground and submitted to the action of pervasive solutions, washing or depositing chemical elements in the ceramic. It is not easy to note such evidence of chemical contamination. Resorting to museum or collectors' objects, such as FUL 32, the only object never to have been buried, cannot be considered since the object was not submitted to XRF analysis. Neither it is possible to resort

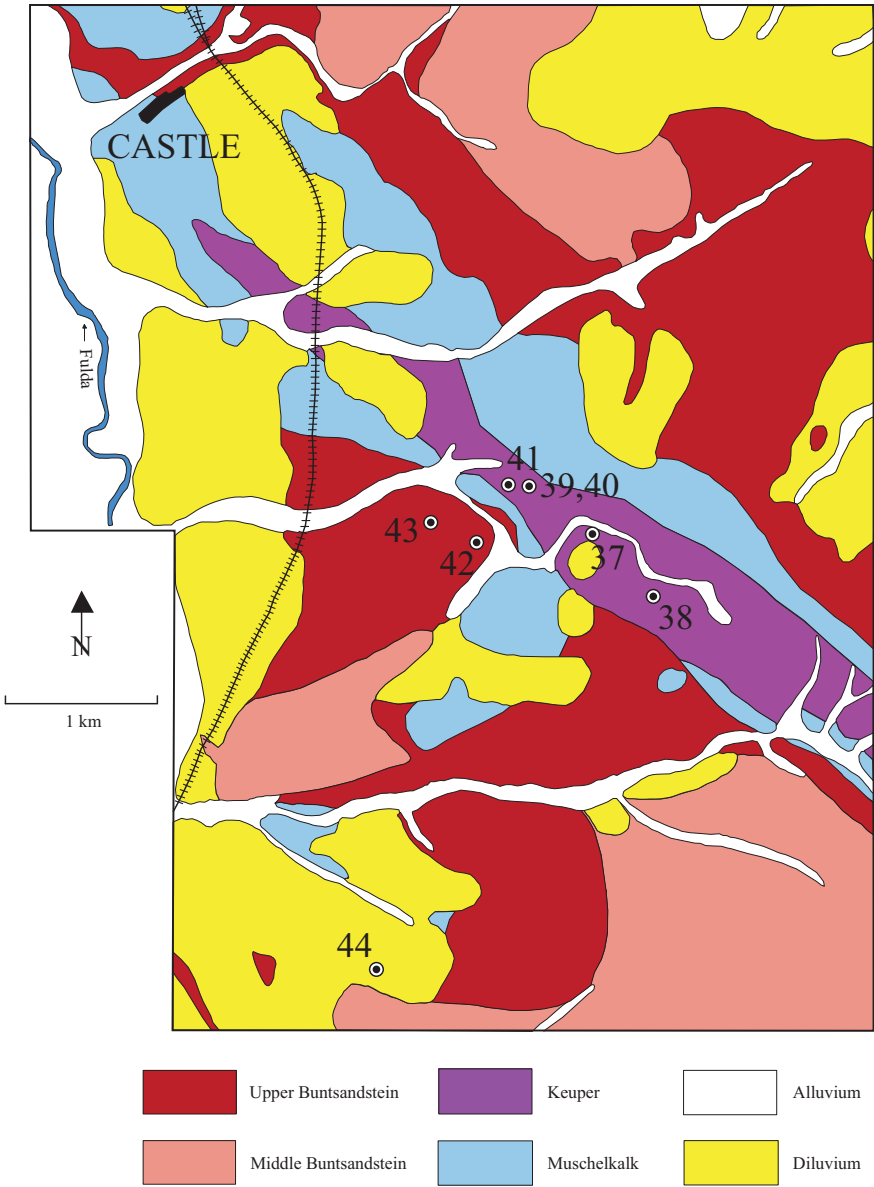


Fig. 3. Simplified geological map of the region Southwest of Fulda (Bücking, 1912). Encircled points = sites of the prospected clays. The castle with the faïence manufacture is shown in black.

to the comparison with local clays, seeing the blend of clays (cf. infra). We must therefore establish the fact that the concentration in oxides and chemical elements generally considered to be mobile (i.e. MnO, Na₂O, Ba etc.) does not seem to be too far dispersed or to reach values much greater than the usual ones. However, special attention deserves the fact that the ceramics are richer in P₂O₅, Pb, Zn, Nb and Sr than the clays.

The great majority of the specimens studied have comparable or slightly higher P₂O₅ concentration than the local clays studied, with three exceptions, FUL 2, FUL 4 and FUL 31. Their phosphorous is

significantly higher than the maximum value of 0.35 wt.% P₂O₅ found in the local clays. Admixing of P-rich material (e.g. fired bones) before firing and postfiring contamination (e.g. burial contamination through migrating P-rich solutions) are two processes normally advocated to explain such P-anomalies (Collomb and Maggetti, 1996, and literature therein). However, no such processes took place for these three shards, as shown by SEM images (Fig. 5c), revealing non-porous P-rich crystals (calcined bones have a characteristic porous structure; Maggetti and Ramstein, 2005) with a chemical composition close to the mineral apatite (Fig. 5, Table 4). These crystals are interpreted as primary phases,

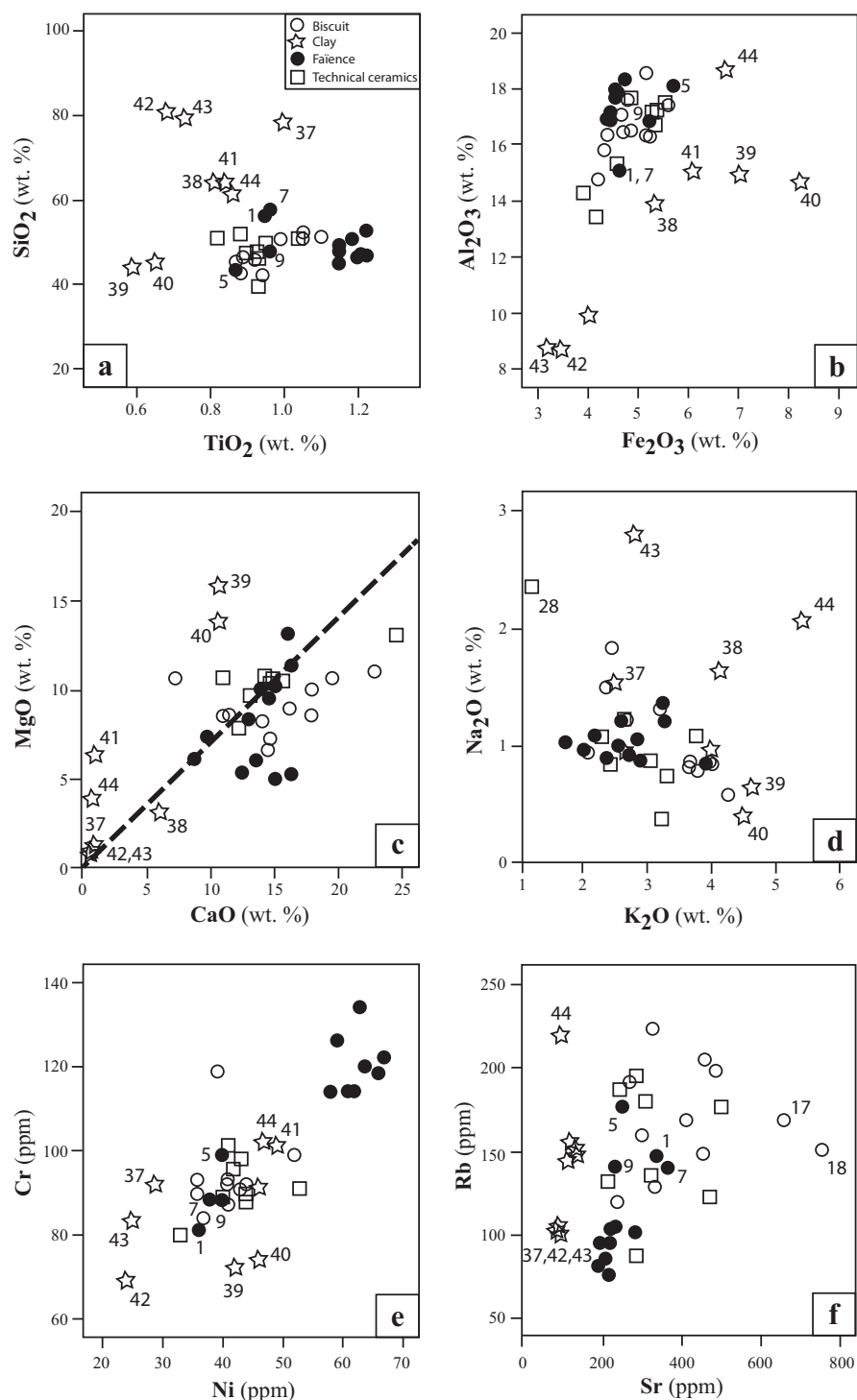


Fig. 4. Body (bulk) compositions for the analysed objects and clays displayed on bivariate plots. Stippled line in (c) = dolomite line.

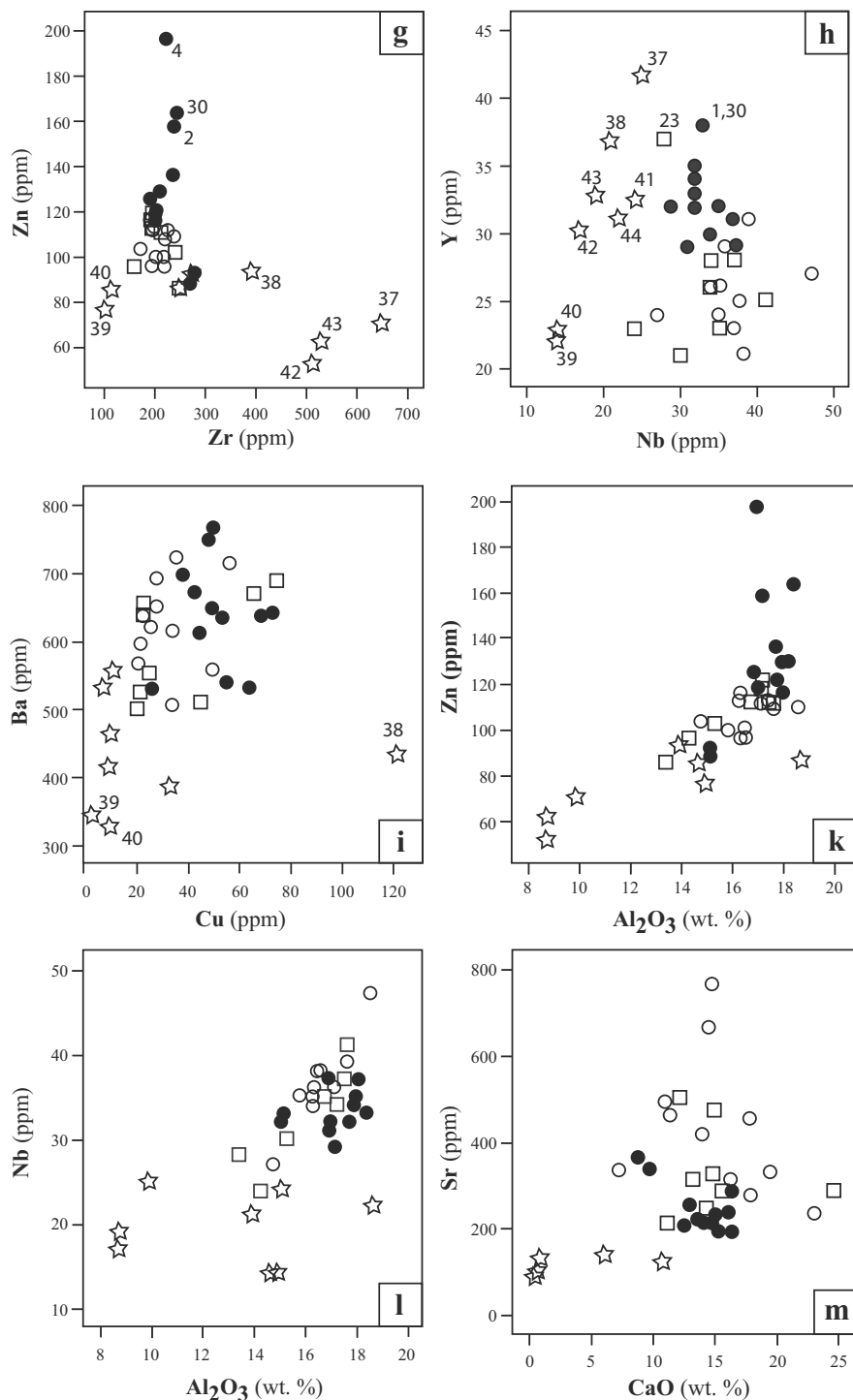


Fig. 4 (continued).

present in the clay *ab initio*. Such P-rich domains can be found as phosphoritic layers of the Lower and Upper gypsiferous marls of the Middle Keuper (Seidel, 2003, pp. 368, 370), but they haven't been found by the prospection.

Local clays contain less than 35 ppm of Pb, but each of the analysed ceramic objects shows a much higher concentration. This can be due to: (1) an insufficient removal of the lead glaze before milling; (2) an infiltration into the porous body by the lead-rich watery suspension obtained during the removal of the lead glaze; (3) an infiltration of the porous biscuit body by the watery glaze suspension during glazing; (4) an infiltration of the porous biscuit body by the fused glaze during firing; and

(5) a contamination of the porous biscuit body by Pb-vapours during firing. We exclude the first hypothesis, as the removal was carefully made. With respect to the other four possibilities, it is impossible to discern which effect(s) is (are) responsible for this contamination.

The positive correlation of zinc and niobium with aluminium (Fig. 4k, l) is evidence that these two trace elements are fixed in the network of clayey minerals present in the raw materials. On the other hand, a fixation of Sr in the calcite/dolomite network cannot be proved through lack of a positive Sr/CaO correlation (Fig. 4m). In this case, post-firing contamination effects could be envisaged, but the copper-rich FUL 32 clay (Fig. 4i) underlines the need for caution against always

Table 3

Bulk compositions of 39 specimens analysed by XRF and one (FUL 32, mean of 4 area measurements 1.2×1.0 mm) by SEM-EDS. Oxides and LOI in wt.%, elements in ppm. Fe_2O_3 = total Fe as Fe_2O_3 .

No. An.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Ba	Cr	Cu	Nb	Ni	Pb	Rb	Sr	Y	Zn	Zr	SUM	LOI
<i>XRF</i>																							
FUL 1	56.10	0.95	15.12	4.63	0.06	7.39	9.75	1.36	3.26	0.20	539	81	55	33	36	3816	147	338	38	88	271	99.36	0.76
FUL 2	49.36	1.15	17.15	4.48	0.12	4.97	15.07	1.00	2.56	2.62	613	114	45	29	58	3834	105	231	32	158	242	99.03	1.69
FUL 3	46.52	1.20	17.73	4.56	0.11	10.19	15.16	0.97	2.02	0.32	636	120	53	32	64	5396	95	193	33	121	205	99.46	0.89
FUL 4	47.40	1.15	16.95	4.42	0.17	5.26	16.33	0.92	2.73	3.23	752	114	49	31	61	2973	101	284	29	197	226	99.05	2.67
FUL 5	47.96	0.96	18.09	5.72	0.07	8.36	12.97	1.21	3.28	0.22	530	99	26	37	40	4049	177	254	29	129	212	99.41	0.90
FUL 6	46.96	1.21	17.91	4.61	0.11	10.02	14.00	0.89	2.37	0.57	766	118	50	34	66	2883	95	213	30	116	204	99.13	1.38
FUL 7	57.85	0.96	15.07	4.65	0.06	6.12	8.70	0.85	3.91	0.43	699	88	38	32	38	3973	140	364	35	92	278	99.19	4.13
FUL 8	44.82	1.15	16.98	4.48	0.15	11.35	16.41	1.03	1.75	0.29	638	114	69	32	62	8033	81	192	34	118	201	99.39	1.01
FUL 9	43.54	0.87	16.83	5.25	0.07	13.13	16.11	0.87	2.90	0.38	531	88	64	37	40	4023	141	235	31	125	194	100.50	1.61
FUL 10	46.65	1.22	17.95	4.57	0.11	9.55	14.64	1.09	2.18	0.79	642	122	73	35	67	5053	77	210	32	129	209	99.44	1.75
FUL 11	46.89	0.89	16.28	5.25	0.07	8.88	16.25	0.79	3.78	0.17	566	87	21	35	41	138	159	304	24	113	199	99.43	11.76
FUL 12	42.56	0.88	16.52	4.89	0.05	10.55	19.52	1.50	2.37	0.19	616	90	34	38	36	117	223	328	25	96	196	99.21	7.49
FUL 13	51.21	1.10	18.54	5.19	0.06	10.66	7.31	0.82	3.65	0.22	641	91	23	47	43	140	129	333	27	109	239	98.95	10.58
FUL 14	50.84	1.05	17.62	4.81	0.05	8.57	11.38	1.31	3.21	0.22	597	93	22	39	36	341	204	463	31	108	224	99.29	1.08
FUL 15	45.81	0.92	16.47	4.73	0.05	8.51	17.91	0.86	3.68	0.23	625	84	25	38	37	146	149	453	21	100	204	99.37	10.29
FUL 16	51.83	0.88	15.28	4.61	0.07	9.66	13.21	0.87	3.04	0.18	513	89	45	30	40	346	180	311	21	102	240	99.83	2.20
FUL 17	50.70	0.99	16.35	4.42	0.05	6.60	14.51	0.58	4.26	0.30	692	88	28	36	40	203	169	662	29	96	218	99.00	10.93
FUL 18	50.78	0.99	15.81	4.35	0.05	7.26	14.78	0.85	4.02	0.36	724	92	36	35	41	262	150	760	26	99	218	99.50	12.00
FUL 19	51.90	1.05	17.10	4.68	0.05	8.54	11.03	1.84	2.47	0.24	649	119	27	36	39	315	198	489	29	111	226	99.13	1.30
FUL 20	42.02	0.94	14.78	4.21	0.15	10.98	22.98	0.94	2.09	0.22	714	99	57	27	52	686	120	234	24	103	175	99.56	9.00
FUL 21	48.08	0.94	17.41	5.62	0.07	8.19	14.11	0.86	3.99	0.16	559	92	50	37	44	70	169	417	23	112	201	99.61	10.20
FUL 22	45.28	0.87	16.32	5.19	0.07	9.95	17.93	1.22	2.69	0.14	506	93	34	34	41	1202	191	272	26	115	198	99.93	4.94
FUL 23	50.93	0.82	13.40	4.19	0.06	10.59	15.00	1.08	2.29	0.32	671	80	66	28	33	4099	123	471	37	86	251	99.27	4.69
FUL 24	45.96	0.93	17.18	5.29	0.07	10.44	15.74	1.23	2.65	0.17	642	96	23	34	42	693	195	283	26	117	195	99.91	3.37
FUL 25	47.31	0.90	16.72	5.35	0.07	10.34	14.76	0.74	3.30	0.16	555	88	25	35	44	108	135	324	23	112	199	99.83	11.37
FUL 26	49.34	0.95	17.50	5.57	0.07	10.69	11.03	0.38	3.22	0.14	525	90	22	37	44	167	132	215	28	111	210	99.07	8.82
FUL 27	39.53	0.93	14.28	3.95	0.19	12.97	24.65	0.84	2.42	0.26	689	91	75	24	53	1093	87	285	23	96	161	100.28	15.61
FUL 28	47.46	0.93	17.24	5.37	0.07	10.72	14.44	2.35	1.16	0.14	502	98	20	34	43	385	187	245	28	120	198	100.07	1.75
FUL 29	50.79	1.04	17.66	4.87	0.05	7.86	12.20	1.08	3.77	0.26	652	101	23	41	41	711	176	503	25	111	223	99.86	3.56
FUL 30	52.38	1.22	18.38	4.74	0.10	5.36	12.48	1.21	2.61	0.76	648	126	50	33	59	8583	86	205	38	163	247	100.27	1.22
FUL 31	50.72	1.18	17.70	4.59	0.10	6.02	13.57	1.06	2.85	1.69	673	134	43	32	63	3607	103	220	32	136	238	100.03	1.54
FUL 37	78.35	1.00	9.89	4.01	0.12	1.08	0.68	1.53	2.50	0.20	416	92	9	25	29	32	98	102	42	70	648	99.51	5.97
FUL 38	64.23	0.81	13.90	5.34	0.14	3.10	5.96	1.64	4.14	0.30	435	91	121	21	46	31	149	138	37	93	392	99.72	11.59
FUL 39	44.04	0.59	15.24	7.07	0.11	16.04	10.88	0.26	4.64	0.21	316	69	4	14	45	8	153	118	21	77	98	99.20	17.66
FUL 40	45.22	0.65	15.00	8.28	0.10	14.05	10.79	0.27	4.48	0.29	355	71	9	13	45	9	147	124	25	88	122	99.24	17.14
FUL 41	64.19	0.84	15.29	6.13	0.18	6.45	0.95	0.45	4.03	0.21	398	90	33	22	52	33	145	130	29	91	249	98.88	10.76
FUL 42	80.93	0.68	8.69	3.46	0.09	0.79	0.40	0.95	2.65	0.16	462	69	10	17	24	28	102	89	30	52	508	98.94	4.14
FUL 43	79.22	0.73	8.73	3.19	0.11	0.82	0.48	2.79	2.81	0.20	557	83	11	19	25	34	104	93	33	62	528	99.22	4.46
FUL 44	61.43	0.86	18.66	6.78	0.06	3.93	0.64	2.06	5.44	0.11	534	102	7	22	47	21	219	95	31	86	248	100.11	5.67
<i>SEM-EDS</i>																							
FUL 32	50.1	1.0	15.6	5.1		8.4	16.9		2.0							0.8						100.00	

explaining such anomalies by a burial contamination – raw materials also can display chemical anomalies. Apart from lead, none of the studied objects seems to have suffered from important contamination effects.

4.2. A new reference group

At first sight, biscuits, faïences and technical ceramics seem to be homogeneous from a chemical point of view. This includes the SEM-EDS analysis of FUL 32. But a more careful analysis brings out a division into two groups, one containing all biscuits, technical ceramics and four faïences (FUL 1, 5, 7, 9) and a second containing the other eight faïences. This differentiation can be noted in the binary diagrams SiO₂/TiO₂ and Cr/Ni in which the first group has less titanium, chromium and nickel. But a Fulda origin of the four faïences from the first group cannot be contested in view of their chemical composition similar to the technical ceramics, objects with a reliable local origin. On the other hand, the eight faïences from the second group could come from another manufacture. This hypothesis is highly unlikely as the group contains dated plant pots of the same mould and decoration as those of the first group. Such chemical differences can likely be explained by the use of clays from levels with different chemical composition, or a different recipe. Consequently, the analyses form a reference group, the first from a German manufacture, easily distinguishable from the other two magnesian manufactures that we know from the Northeast

of France, i.e. Granges-le-Bourg (Maggetti et al., 2009a; Maggetti, 2013) and Lunéville (Maggetti et al., in press), even though the Fulda objects are clearly more inhomogeneous (Fig. 6). This probably indicates a less thorough attempt at homogeneity than in the two French manufactures.

4.3. Technical aspects

Age related chemical differences of the clays are exemplified in Fig. 4. The *Upper Buntsandstein* clays FUL 42 and 43 are for instance rich in SiO₂ and Zr, but low in Al₂O₃, Fe₂O₃, Cr and Ni. Both *Keuper* samples taken at a significant depth (FUL 39, 40) have very high MgO values and contain dolomite, whereas both *Upper Buntsandstein* clays and one superficial *Keuper* clay (FUL 37) are MgO-poor with no dolomite (Fig. 4c). The *Diluvial* clay FUL 44 and two superficial *Keuper* clays (FUL 38, 41) have intermediate MgO and no dolomite either. If the geological map is correct, one has to consider that superficial strata of the *Keuper* marls were de-carbonated by meteoric waters, as assumed for the raw materials from Granges-le-Bourg, where the original MgO- (and CaO-) concentrations were only found at a depth of 0.6–0.7 m (Maggetti et al., 2009a; Maggetti, 2013). Furthermore, not all MgO is fixed in the dolomite phase, as evidenced by FUL 39, 40, 41 and 44, which is plot in Fig. 4c higher than the dolomite line, i. e. with not enough CaO to combine all MgO into this mineral. It is therefore likely that the excess MgO is present in another discrete phase (Smectite or

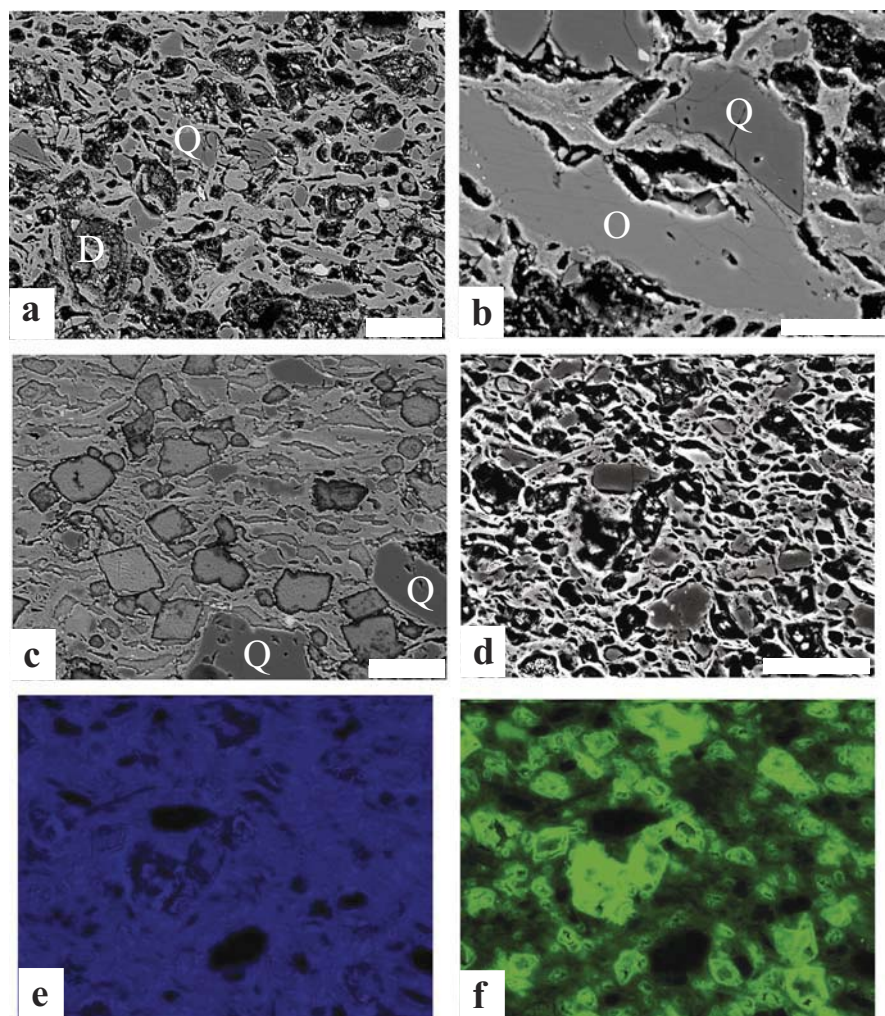


Fig. 5. SEM backscattered electron images of: (a) body showing quartz (Q) in a well vitrified matrix. Voids are former dolomitic grains (D) as shown by the magnesium concentrations. Calcium is more evenly distributed throughout the matrix. Faïence FUL 10. Bar 20 μm ; (b) orthoclase (O) and quartz crystals. The former doesn't show any signs of melting. In the matrix tiny newly formed crystals (calcisilicates) can be seen. Faïence FUL 10. Bar 10 μm ; (c) phosphor-rich rhomboedric shaped crystals in a less porous part of faïence FUL 31. Bar 20 μm ; (d) other aspect of FUL 10. Bar 50 μm ; (e) Ca map of (d) showing even distribution; (f) Mg map of (d) with Mg concentrated in voids = former dolomite grains.

illite?). The phase association as determined by XRD is in good agreement with the microscopical results.

The prospecting did not succeed in finding adequate clays which could have been used as they were. This is not surprising as 18th century faïence potters worked with a blend of purified clays, as summarized by Maggetti (2012) for the French workshops. Consequently, one can

surmise that the Fulda manufacture proceeded in the same manner, mixing one or several clays, one of which would have been MgO rich, much like the dolomitic marls of the *Keuper*. The generally higher contents in alumina of the ceramics compared to the clays indicate decantation processes which increased the Al_2O_3 -rich clay fraction. If one considers the composition of the untreated clays, it is clear that those

Table 4
SEM-EDS analyses of P-rich sample FUL 31 normalized to 100 wt.% (n = number of individual analyses in the average results).

An. Nr.	Area	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
Whole body											
FUL 31 (4)	2 × 1.5 mm		4.1	18.0	51.6	1.6	0.1	2.6	15.5	1.0	5.6
P-poor domain											
FUL 31-25	150 × 180 μm		3.6	17.4	56.3	0.3	0.5	3.5	12.0	1.4	5.0
FUL 31-26	400 × 350 μm		4.8	19.1	51.2	0.6	0.6	3.0	13.7	1.4	5.6
P-rich domain											
FUL 31-16	200 × 150 μm	0.1	2.8	16.3	37.4	13.4		2.3	23.1	0.7	3.9
FUL 31-17	500 × 400 μm		3.1	15.4	41.1	12.0		2.7	20.5	0.8	4.4
P-rich crystals											
FUL 31-18	10 × 5 μm	0.1	0.1	0.8	0.6	43.3		0.2	54.7		0.2
FUL 31-19	5 × 5 μm		0.5	2.2	1.4	42.4		0.2	52.4		0.9
FUL 31-27	25 × 25 μm	0.2	0.3	1.2	1.2	43.3	0.6		52.6		0.6
Apatite (F 3.8/Ca 4)						45.8			54.2		

of the *Upper Bundsandstein* are too rich in SiO_2 and that the decarbonated superficial clays do not have the chemical composition suitable for the mixture. These clays would need to be experimentally treated and then analysed in order to see which could have been used — a project beyond the present study.

As accots were used only once, one understands why the potters made them with the faïence paste at hand and not with a specific refractory mixture. However, saggar pins had to be resistant at high temperatures, go through as many firing cycles as possible, and bear the weight of the ceramic object. Therefore one would expect the use of refractory mixtures with a high mechanical resistance and low $\text{CaO} + \text{MgO}$, but this is obviously not the case. High CaO and MgO pastes of saggar pins were also reported from the faïence manufactures of Fribourg (Blanc, 2007) and Granges-le-Bourg (Maggetti et al., 2009b). Such recipes are puzzling and not well understood.

According to their body colours, the studied objects were fired in dominating oxidizing atmospheres. The ancient firing temperatures can be estimated by comparison of the faïences' phase associations with the phase evolution in experimentally fired dolomitic marls of similar mineralogical and chemical composition (Peters and Jenni, 1973; Maggetti, 1979, 2013; Jornet, 1982; Shoval, 1988; Benghezal, 1989, 1994; Béarat, 1992; Échallier and Méry, 1989, 1992; Mumenthaler et al., 1995; Duminuco et al., 1998; Maggetti et al., 2009a; Trindade et al., 2009). For association (a), inferred temperatures were most probably around 800–900 °C (gehlenite in around 800 °C, illite/muscovite out above 900 °C). They were in the range of 900–1050 °C for association (b), as no illite was detected and as marls will show extensive

fusion at 1100 °C (Küpfer and Maggetti, 1978). These temperature estimations are in good agreement with those derived from microstructural observations, as FUL 3, 10, 32 can be classified as “advanced initial vitrification” and LNV 2, 19 and 20 as “advanced extensive vitrification”, which develop at firing temperatures of about 900–1000 °C (Maniatis and Tite, 1981; Kilikoglou, 1994; Wolf, 2002). Such temperatures fall in the usual range of the French faïence kilns of the 18th century (Rosen, 1995; Maggetti, 2007, 2012). Association (a) contains biscuits, technical ceramics and one faïence, whereas the remaining samples, i.e. mostly all faïences, pertain to association (b). This result is not surprising, as biscuits were generally fired at lower temperatures than the faïences, the latter being fired twice.

5. Conclusions

The faïences from Fulda are rich in MgO , pointing to the use of Triassic dolomitic marls. It can be deduced that the products from other German manufactures, situated as Fulda on a Triassic subsoil (Fig. 1), should also have a magnesian nature. A peculiarity of Fulda's faïence bodies is phosphor-rich relicts of the original clay. This is the first description of primary P_2O_5 concentrations in ceramics. Fulda's faïence forms a new chemical reference group, easily distinguishable from the two currently known French MgO -rich groups. These chemical differences can be explained by the use of different MgO -rich clays in each manufacture: *Middle Muschelkalk* for Granges-le-Bourg, for Fulda and *Middle Keuper* for Lunéville. Even though the technique used in Fulda is not very different from that of the French manufactures

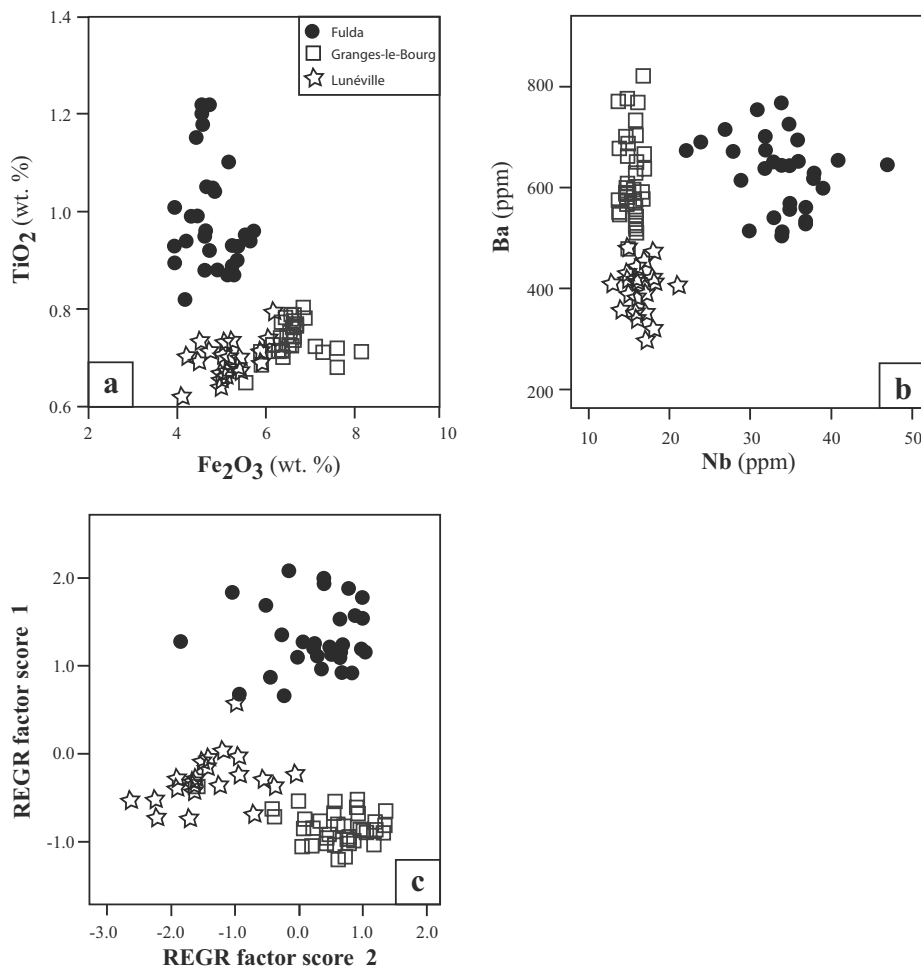


Fig. 6. Differentiation of MgO -rich faïence reference groups from Fulda (this work), Granges-le-Bourg ($n = 38$, Maggetti et al., 2009a) and Lunéville (manufacture of Jacques II Chambrette, $n = 25$, Maggetti et al., in press) in two binary plots showing the most discriminating oxides and elements (a, b) and in a factor analysis (c).

(blend of clays, purification process, oxydating firing in two steps at maximum temperatures of 900–1050 °C), it would seem that the raw materials were not processed as well as in France.

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